

# ORDERED ARRAY OF MAGNETIZED NANORODS AND ASSOCIATED METHODS

## Related Application

This application claims priority from co-pending provisional application Serial No. 60/455,349, which was filed on March 17, 2003, and which is incorporated herein by reference in its entirety.

5

## Field Of The Invention

The present invention relates to the field of magnetic media and, more particularly, to an ordered array of magnetized nanorods and its associated methods.

10

## Background Of The Invention

Thin films of magnetic materials are important in mass data storage technology. Today's best "hard drives" are able to store approximately 100 Gbytes of information on a 3.5 inch (double-side) disk. Such a density

- 15 corresponds to  $4.2 \times 10^{10}$  bits per in<sup>2</sup> or a bit size of about 120 nm. Each bit is a magnetic domain, often a particle, capable of being magnetized in a certain direction for future readout. Magnetic disk technology (and other areas, including VLSI fabrication with ever decreasing line widths) faces some "physics-dictated" (rather than technique-dictated) limits. Specifically, when
- 20 magnetic domains become too small, any alignment of spins by an external magnetic field is lost when the field is removed. At this superparamagnetic/ferromagnetic limit (which corresponds to a characteristic size of about 10 nm for Ni at room temperature) because the domains/particles are no longer able to sustain a permanent magnetic dipole
- 25 (ferromagnetism), the material is not useful for magnetic storage.

One method to push the superparamagnetic limit beyond the  $10 \times 10^{10}$  bits per in<sup>2</sup> barrier is to prepare "perpendicular" media, where anisotropic bits are magnetized perpendicular to the surface. Such highly anisotropic high aspect ratio particles exhibit perpendicular ferromagnetic behavior at

diameters less than a spherical particle of the same diameter. This property permits a denser packing of ferromagnetic particles in the plane of the recording medium (i.e. a greater storage density). Other storage density advantages accrue from the fact that the particles will be also uniform in size

5 and distribution. Uniformity in size means that no particle will be below the ferromagnetic limit.

- Noteworthy advantages will be realized from the readout perspective. Small currents are induced in the readout head as it passes over magnetized bits. Relatively uniform spacing helps to ensure uniformity in readout current.
- 10 The read head will encounter one identical particle, with predictable response, at a time, instead of various-size clumps of particles. A final significance of the disclosed magnetic material is also related to read-out: in order to be able to read individual bits, the read head must approach the disk surface as closely as possible, a requirement which is, itself, a challenge in lubrication (to prevent crashes). Anisotropy in the read head response and in the magnetic field of the particles are refinements which permit detection of closely-spaced bits. Rodlike particles, oriented and magnetized as described below, provide enhanced magnetization in the direction perpendicular to the disk surface, which facilitates readout. It is estimated that the advantages above, when
- 15 taken in totality, will lead to an improvement in storage density of at least a factor of ten.

- 20 An array of uniform, high aspect-ratio rods has many potential applications other than magnetic storage. It is extremely difficult to produce uniform "columns" by photolithography. Tall features are subject to
- 25 undercutting during the etching phase. While hairlike nanostructures, such as carbon nanotubes, may be grown from surfaces, they are not arranged in an array pattern. In addition, the nanorod arrays herein disclosed may be used as "masters" for preparing arrays of holes in softer materials, either by microcontact stamping or by molding (e.g. with rubbery polymers such as

polydimethylsiloxane). Such applications illustrate further uses of the invention.

### Summary Of The Invention

With the foregoing in mind, the present invention advantageously provides an ordered array of magnetized nanorods, comprising a plurality of metallic nanorods generally cylindrical in shape and including a first metal portion coated with a positively charged polyelectrolyte and a second metal portion coated with an alkanethiolate. A layer of a hardened polymer holds the plurality of nanorods by each individual nanorod having said second metal portion embedded therein so that the first metal portion extends away from the layer of hardened polymer, and wherein said plurality of metallic nanorods is ordered in the array by having substantially all individual nanorods of the plurality of nanorods oriented generally parallel to each other. The ordered array preferably includes each individual nanorod having a length of between approximately 1 and 10  $\mu\text{m}$  and a width or diameter of between approximately 20 to 200 nm. Most preferably, the ordered array of nanorods has an inter-nanorod spacing of between approximately 10 to 200 nm. A preferred first metal in the invention is nickel and a preferred second metal is gold.

Method aspects of the invention include a method of making an ordered array of magnetized nanorods. The method comprises electroforming a plurality of relatively high aspect ratio nanorods wherein each individual nanorod includes a portion electroformed of gold and a portion electroformed of nickel. The skilled should understand that the terms "electroforming" and "electrodeposition" are used synonymously herein. Following electroforming, the method includes modifying the plurality of nanorods so that in each individual nanorod the gold portion is modified to become hydrophobic and the nickel portion is modified to become hydrophilic. The method then calls for dispersing the plurality of modified nanorods on an interface between an aqueous phase and a non-aqueous phase so that each individual nanorod orients having the hydrophilic nickel portion in the aqueous phase extending away from the interface in a relatively perpendicular direction therefrom and having the hydrophobic gold portion in the non-aqueous phase extending

away from the interface in a relatively perpendicular direction therefrom. Finally, the method comprises self-assembling the plurality of dispersed nanorods by adjusting ionic content in the aqueous phase so as to sufficiently influence repulsive forces between individual nanorods of the plurality of 5 nanorods to thereby promote self-assembly of the plurality of nanorods into an ordered array wherein substantially all individual nanorods of the plurality are aligned generally parallel with each other along the interface.

#### Brief Description Of The Drawings

- 10 Some of the features, advantages, and benefits of the present invention having been stated, others will become apparent as the description proceeds when taken in conjunction with the accompanying drawings, presented for solely for exemplary purposes and not with intent to limit the invention thereto, and in which:
- 15 FIG. 1 shows top plan and side elevation views of the nanorod array according to an embodiment of the present invention;
- FIG. 2 illustrates electroforming or electrodeposition of the nanorods within pores of a membrane filter, preferably an aluminum oxide (alumina) membrane;
- 20 FIG. 3 is an electron micrograph view of nickel nanorods according to the invention;
- FIG. 4 shows modification or derivatization of the nanorods according to the method of the invention; and
- 25 FIG. 5 depicts polymerization of a non-aqueous phase to fix in place the ordered array of nanorods according to the invention.

#### Detailed Description of the Preferred Embodiment

- The present invention will now be described more fully hereinafter with reference to the accompanying drawings, in which preferred embodiments of 30 the invention are shown. Unless otherwise defined, all technical and scientific

terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention pertains. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, suitable methods and materials 5 are described below. Any publications, patent applications, patents, and other references mentioned herein are incorporated by reference in their entirety. In case of conflict, the present specification, including any definitions, will control. In addition, the materials, methods and examples given are illustrative in nature only and not intended to be limiting. Accordingly, this invention may be 10 embodied in many different forms and should not be construed as limited to the illustrated embodiments set forth herein. Rather, these illustrated embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the invention to those skilled in the art. Other features and advantages of the invention will be apparent from 15 the following detailed description, and from the appended claims.

The general structure of the ordered array **10** of nanorods according to the present invention is shown in FIG. 1, which depicts side and top views of a representative self assembled array at a water/air interface. Magnetic

5 nanorods **12** have been produced before, but they, and other particles with a high aspect ratio, such as a plates, have been generally ordered with the long dimension parallel to the interface surface. An important structural feature of the present invention, illustrated in FIG. 1, is that the particles are oriented perpendicular to the interface. The particles, termed herein "nanorods" **12**,

10 are generally cylindrical with a diameter ranging from approximately 20-200 nm, and a length of approximately from 1-10  $\mu$ m inter-nanorod spacing of 10-200 nm is preferred in the ordered array. The force which drives the nanorods to the interface is the hydrophobic nature of one end of the nanorods (they are amphiphilic, in fact) and the force which causes

15 self-assembly into an array is the mutual electrostatic repulsion between particles. A hexagonal close-packed array is expected to be the lowest energy configuration in the presence of repulsive interactions.

A method of making the nanorods includes producing of generally uniform high aspect ratio nanorods **12** modifying the nanorods such that one 20 end becomes hydrophobic and the other end becomes hydrophilic; dispersing the modified nanorods at the interface **14** of an aqueous phase **16** and a water-immiscible non-aqueous phase **18** and self-assembling by controlling the order-inducing repulsive interactions between interfacial nanorods **12** until self assembly is achieved. The self-assembly may be monitored *in situ* as it 25 occurs. Following completion of self-assembly, the array may be hardened in place by polymerization of the non-aqueous phase **18**.

Production of nanorods **12** is preferably accomplished by electrochemical deposition, or electroforming, during which metallic nanorods are grown in the pores of commercially available alumina membrane filters as 30 known to those skilled in the art. The process is generally illustrated in FIG. 2.

First, a thin gold film is evaporated on one surface of an aluminum oxide alumina filter **20** that comprises 20-200 nm diameter pores. Following immersion in the appropriate electroplating bath, gold, is deposited in the pores. The process is repeated for nickel. The length of the rod is controlled

5 by the electroplating time and current. The alumina membrane **20** template is then dissolved in base to yield free nanorods **12**. FIG. 3 shows a sample of nickel nanowires grown according to the method of the invention. The skilled should recognize that in order to keep the aspect ratio at about 10:1 (length:diameter) it is preferable to plate for much shorter times than was

10 done for making the example shown in FIG. 3.

Modification of nanorods. Rods **12** will be approximately half gold (inert) and half nickel (less inert). A native oxide layer will spontaneously form on the surface of the nickel portion **22** on exposure to air. The nanorods **12** are exposed to a solution of octadecanethiol in ethanol, which causes a layer

15 of octadecanethiolate to spontaneously adsorb on the surface. The interaction of thiol with the gold portion **24** is strong, but with the nickel (oxide) portion it is weak. Thus, the thiol may be washed off the nickel portion **22**. The purpose of the alkanethiol is to render the gold portion **24** of the nanorod **12** hydrophobic. On exposure of the modified, thiol-derivatized nanorods to

20 an aqueous solution of positive polyelectrolyte, such as poly (diallyldimethylammonium chloride) (PDADMAC), the polyelectrolyte will adsorb to the nickel (oxide) portion **22** via electrostatic forces (metal oxide surfaces tend to be negative), rendering the nickel portion hydrophilic.

Dispersion of nanorods. After the previous step, the nanorods **12** will

25 be amphiphilic (have hydrophobic and hydrophilic ends, much like a soap molecule). Thus, they will collect at an interface **14** between air and water, or between an aqueous phase **16** and a non-aqueous water-immiscible phase **18** such as an organic solvent. An aqueous dispersion of nanorods **12** should be dispersible via gentle ultrasound. The fact that the nanorods **12** are

positively charged at one end also aids in separating individual nanorods from each other. The hydrophilic ends will reside in the aqueous phase **16** and the hydrophobic ends will reside in the non-aqueous phase **18**, be it an air or organic solvent phase, as depicted in FIG. 1 (the fact that the modified

5 nanorods float upright on the water surface leads us to call them "nanobuoys"). The number of nanobuoys per unit area is controlled by the number of nanorods or by the area over which they are dispersed. The original alumina membranes **20** from which the nanorods **12** are templated have pore densities roughly similar to the targeted coverage for the

10 nanobuoys.

Self-assembly of the ordered array by controlling repulsive interactions. Nanorods **12** will have weak intermolecular (van der Waals) interactions and somewhat stronger magnetic interactions that will tend to agglomerate them. Countering these attractive forces are strong, long-range electrostatic

15 repulsive forces between the positively-charged nickel ends and the strong tendency for nanorods **12** to accumulate at the interface **14**, where both hydrophilic and hydrophobic ends are in their preferred environments. Repulsive interactions are required to separate the nanorods **12** and to force them into the ordered array (the "self assembly" process). The magnitude of

20 the repulsive forces depends on the strength of the electrostatic fields emanating from the Ni ends (charged) of the nanorods **12**. These fields are controlled with the addition of salt (small ionic species) to the aqueous phase. At high salt concentration, the electric fields are substantially screened and the interactions are minimized. For example, the ranges of these fields in

25 solution of  $10^{-4}$  and  $10^{-5}$  M NaCl are about 30 nm and 300 nm, respectively.

Monitoring self-assembly. The end product of the method is a relatively rugged material that is easily subjected to microscopy to infer ordering. The nanorods being ordered are of high refractive index, so for particle spacings that are close to or larger than the wavelength of light (e.g. 400 nm for a blue laser) it is possible to observe ordering *in situ* with the aid of a small laser

- directed upwards through the bottom of the container and perpendicular to the interface and to the self-ordering array, producing a diffraction pattern on a plane (screen) above the container. Diffraction patterns may be measured and converted to spacings between nanobuoys. Alternatively, diffraction
- 5 patterns may be collected with a CCD and Fourier transformed to produce a real-space image of the array. It is assumed that a hexagonal close packed array will allow nanobuoys to space themselves as far apart from each other as possible, but other structures may also exist, particularly at the limit of very high and very low repulsions.
- 10 Hardening the system. Without some method for fixing the arrayed nanorods **12** in place the system would remain unstable. In order to capture the result of the self assembly, the final method step comprises a polymerizable monomer in the non-aqueous organic layer. Methyl methacrylate (MMA) is suitable, for example, as it forms an optically transparent polymer. A small amount of an appropriate azo initiator, of which there is a great variety commercially available, would allow near room temperature conversion of MMA to PMMA, fixing the nanorods in the manner depicted in FIG. 5 so that they are held in place in the ordered array.
- 15

- Characterization. The fixed array may be imaged by scanning probe microscopy (atomic force or, for magnetic particles, magnetic force) to verify its structure, spacing, uniformity and the general quality of the ordered array
10. Additionally, further magnetic measurements, such as SQUID, may be used to further verify the quality of the product.

- In the drawings and specification, there have been disclosed a typical 25 preferred embodiment of the invention, and although specific terms are employed, the terms are used in a descriptive sense only and not for purposes of limitation. The invention has been described in considerable detail with specific reference to these illustrated embodiments. It will be apparent, however, that various modifications and changes can be made

within the spirit and scope of the invention as described in the foregoing specification and as defined in the appended claims.